

CIGS Films Via Nanoparticle Spray Deposition: Attempts at Densifying a Porous Precursor

D.L. Schulz, C.J. Curtis, A. Cram,
J.L. Alleman, A. Mason, R.J. Matson,
J.D. Perkins, and D.S. Ginley

*Presented at the 26th IEEE Photovoltaic
Specialists Conference, September 29B
October 3, 1997, Anaheim, California*



National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado 80401-3393
A national laboratory of
the U.S. Department of Energy
Managed by Midwest Research Institute
for the U.S. Department of Energy
under contract No. DE-AC36-83CH10093

Prepared under Task No. PV705201

September 1997

CIGS FILMS VIA NANOPARTICLE SPRAY DEPOSITION: ATTEMPTS AT DENSIFYING A POROUS PRECURSOR

Douglas L. Schulz, Calvin J. Curtis, Alan Cram, Jeffrey L. Alleman, Alice Mason, Richard J. Matson, John D. Perkins,
David S. Ginley

National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401-3393

ABSTRACT

This report summarizes our recent efforts to produce large-grained CIGS materials from porous nanoparticle precursor films. In our approach, a nanoparticle colloid is first prepared via low-temperature solution synthesis. Next, a thin precursor film is prepared by spray deposition of this colloid onto a heated substrate. Post-processing of these precursors is performed to induce phase formation and grain growth. Various colloids have been sprayed onto substrates such as molybdenum/glass and CdS/SnO₂/glass. Post-processing treatments under controlled gas ambients have been performed according to both standard and rapid-thermal annealing (RTA) approaches. Morphology, phase formation, and chemical composition of these nanoparticle-derived films have been characterized using SEM, XRD, Raman, and AES. Although the majority of the approaches employed did not produce large-grained materials, CIGS colloid sprayed onto CdS/SnO₂/glass substrates heated at 225°C produced films with a dense morphology as-deposited.

INTRODUCTION

Copper indium gallium diselenide, Cu(In,Ga)Se₂ (CIGS), is one of a few candidate thin film materials presently being evaluated as the absorber layer in polycrystalline solar-cell devices. We have recently employed nanoparticle-based precursors in the spray deposition of CIGS materials [1]. This nanoparticle precursor approach differs from standard spray deposition in that the size of the particles that compose the spray deposition "ink" are one or two orders of magnitude smaller in the former (i.e., 10-50 nm) versus the latter (0.5-2.0 µm) resulting in a unique precursor material.

Previously, we have demonstrated a straightforward metathesis reaction to produce methanolic Cu-In-Ga-Se nanoparticle colloids in excellent yield [1]. These amorphous Cu-In-Ga-Se colloids were employed as precursors for the spray deposition of Cu-rich CIGS precursor films. After thermal processing and evaporation of additional Ga, In, and Se, the product CIGS films were comprised of a smaller-grained intermediate layer and a larger-grained top layer. Apparently, the reaction kinetics of nanoparticle-derived Cu-In-Ga-Se precursor films are markedly different than those prepared by evaporation. As a consequence, the thermal treatment methods that are presently producing high-efficiency CIGS solar cells from

evaporated precursors are not amenable toward large-grain CIGS formation in nanoparticle-derived Cu-In-Ga-Se precursor films. Standard I-V characterization showed the solar cells fabricated in this study exhibited large series resistance versus high efficiency cells (i.e., 13 vs. ~0.2 Ω•cm) [1,2]. Large series resistance has also been reported for CIS/CdS solar cells where the CIS layer was fabricated via screen printing [3,4]. The observed limitations in device performance may be a consequence of an intermediate small-grained layer which corresponds to the sprayed nanoparticle layer.

This paper details our attempts to circumvent the aforementioned limitations in device performance through the formation of large-grained CIS from a small-grained porous precursor network. Implicit is the desire to access a liquid-assisted growth regime and thereby form large-grained materials. Accordingly, three different approaches were attempted as follows: (1) incorporate excess Se in the precursor film through the use of a CuSe-containing colloid with the overall stoichiometry "CuInSe_{2.5}"; (2) employ rapid thermal annealing of "CuInSe_{2.5}" precursor films; and (3) utilize a layered CuSe/In₂Se₃/molybdenum composite structure. One additional approach employed was the spray deposition of CIGS colloid onto CdS/SnO₂/glass films according to a reverse backwall solar-cell approach.

EXPERIMENT

The details of the Cu-In-Ga-Se nanoparticle synthesis will be presented elsewhere [5]. In short, nanoparticle colloids were prepared by reacting a mixture of CuI and/or [Cu(CH₃CN)₄](BF₄)₂ and/or InI₃ and/or GaI₃ in pyridine with Na₂Se in methanol at reduced temperature under inert atmosphere. Colloids with the compositions CuInSe_{2.5}, CuSe, In₂Se₃, and Cu_{1.10}In_{0.68}Ga_{0.23}Se_x were prepared as shown in eqs 1-4, respectively.

Precursor films were prepared by spraying purified nanoparticle colloids onto heated molybdenum-coated glass and CdS/SnO₂/glass substrates. Spray deposition of the colloids to form precursor Cu-In-Ga-Se films was performed under inert conditions.

RESULTS AND DISCUSSION

Attempts to produce large-grained CIGS materials were aimed toward accessing a liquid-assisted growth regime. Probst et al. [6] have recently reported two prerequisites

for liquid-assisted growth of large-grained CIS material from an elemental stacked precursor: (1) the processing conditions to support the formation of the CuSe-phase have to be fulfilled; and (2) the reaction kinetics for the formation and for the consumption of CuSe enable a dynamic heating process to exceed the melting point of CuSe before it is consumed completely to CIS. The pertinent chemical equilibrium for the formation of liquid CuSe via the interaction of selenium vapor with Cu₂Se is shown in eq 5. Our approaches geared toward the development of a liquid phase are now described in detail.

Approach 1: "CuInSe_{2.5}" Films

In an attempt to address the first prerequisite of Probst et al. (see above) [6], excess Se was "built" into the precursor colloid through the use of a Cu²⁺ starting reagent, [Cu(CH₃CN)₄](BF₄)₂. Reaction of one mole of this reagent and one mole of InI₃ with 2.5 moles of Na₂Se gives a colloid with the overall stoichiometry "CuInSe_{2.5}", a 25 at.% Se excess. Films 2-3 μm thick were spray-deposited onto Mo-coated glass substrates heated to 225°C. Figure 1a is an SEM micrograph of a "CuInSe_{2.5}"/Mo/glass film as-sprayed illustrating the microporous nature of these nanoparticle-derived precursor films. XRD of this film gave broad reflections that may be a consequence of an amorphous CIS phase. Two CuInSe_{2.5} precursor films were subjected to further treatments. One was annealed at 600°C/20 min under Ar while the other was first compressed in a hydraulic press (1000 kg/cm²) and then annealed. Figure 1b is an SEM micrograph of the latter. It is apparent from this SEM image that bulk liquid-assisted growth was not observed, but, the pressed sample exhibits grain growth at the surface. XRD data for both films were very similar with CIS phase formation observed. (Note: owing to the similarities in crystal structure, it is possible that Cu_{2-x}Se phase coexists with CIS but is not differentiable.) Raman spectroscopy was performed on two different CuInSe_{2.5} samples as a means of following the reaction and determining the phase composition of the precursor that was observed to be amorphous by XRD (see above). Figure 2 shows a Raman curve for two samples: a "CuInSe_{2.5}" film as-sprayed (Fig. 2a) and a "CuInSe_{2.5}" film annealed at 560°C/10 min in Ar (Fig. 2b). The three peaks in the annealed sample (Fig. 2b) can be indexed to Raman active modes of CIS as previously reported [7]. The peak at 128 cm⁻¹ in the as-sprayed sample has not yet been assigned. The utility of Raman spectroscopy as an in-situ and ex-situ tool for

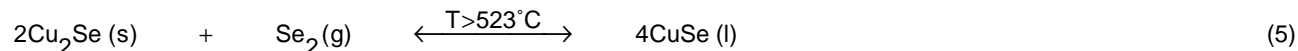
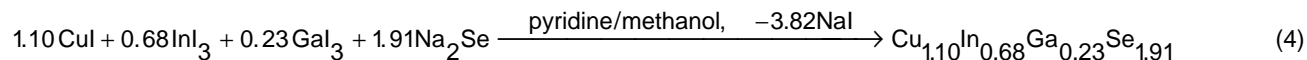
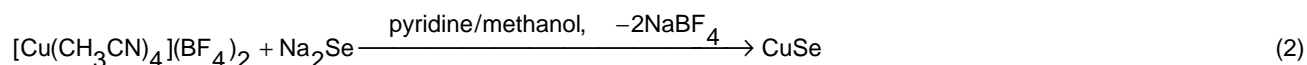
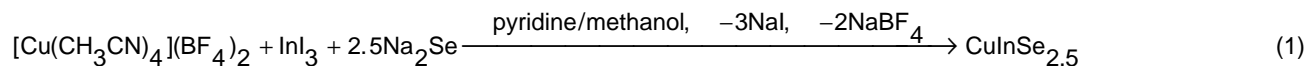
characterizing phase formation in the CIS system is presently being investigated.

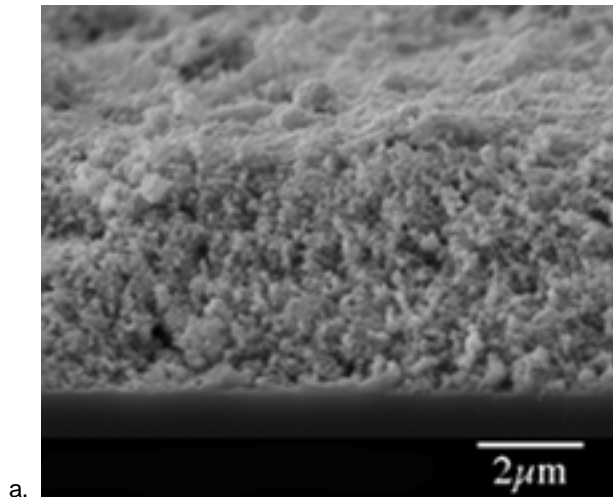
Approach 2: RTA of "CuInSe_{2.5}" Films

In an attempt to address the second prerequisite of Probst et al. (see above) [6], thermal processing of CuInSe_{2.5} films was performed in an RTA furnace. Two films were subjected to RTA in an N₂ atmosphere at 550°C/3 min and 625°C/2 min, respectively. XRD characterization of both films showed CIS phase formation. While SEM characterization again shows no bulk liquid-assisted growth, some evidence of liquid formation was observed on the surface of the 550°C/3 min film as shown in Figure 1c. Modification to the standard RTA is presently underway to provide a means of illuminating from the back- or front-side only.

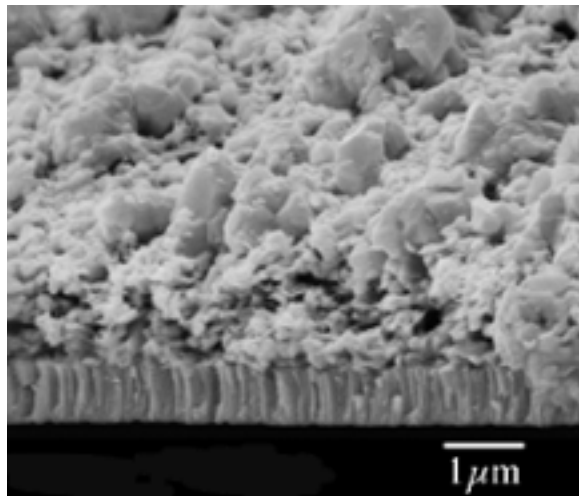
Approach 3: Composite CuSe/In₂Se₃/Mo

Given the inability of RTA to adequately address the second prerequisite of Probst et al., an alternative strategy was pursued. One possible explanation of the RTA result is that the nanoparticles comprising the CuInSe_{2.5} film are atomically mixed and that accessing the liquid phase for an appreciable duration of time is not kinetically favorable owing to the rapid formation of the CIS phase. To test this hypothesis, a bilayer approach was employed whereby first a layer of In₂Se₃ nanoparticles was sprayed onto a Mo-coated glass substrate and then a layer of CuSe nanoparticles was sprayed on top giving the composite structure CuSe/In₂Se₃/Mo. Two such films were subjected to thermal treatments. One was annealed at 600°C/20 min under Ar while the other was first compressed in a hydraulic press (1000 kg/cm²) and then annealed. Again, bulk liquid-assisted growth was not observed by SEM and the pressed sample exhibited larger grains at the surface. Figure 3 is an SEM micrograph of the pressed film illustrating the grain growth in the CuSe surface layer as well as a clear delineation between the two layers even after processing. XRD characterization of these films gave CIS phase formation in the unpressed film and CIS + In₂Se₃ phase formation in the pressed film. We attribute the observation of In₂Se₃ in the pressed film to the fact that the overall stoichiometry of the composite started out quite In-rich and that this excess could not be evolved [presumably as In₂Se (g)] from the pressed film as readily as from the unpressed film.

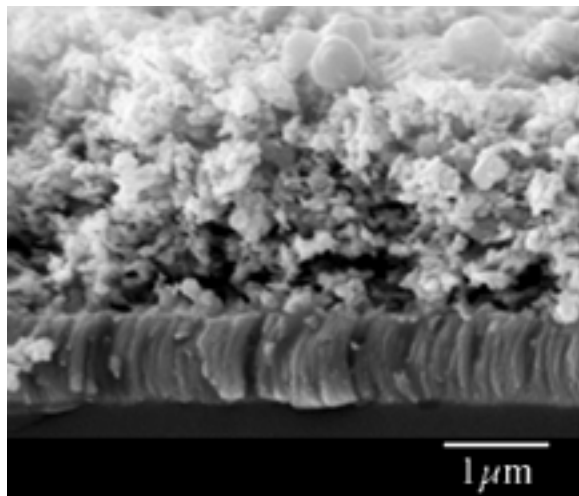




a.



b.



c.

Fig. 1. SEM cross-section micrographs of "CuInSe_{2.5}" films (a) as-sprayed; (b) after pressing and annealing at 600°C/20 min; and (c) after RTA at 550°C/3 min.

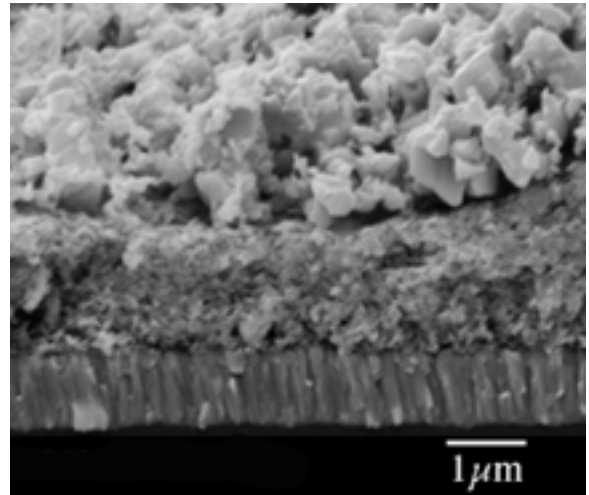


Fig. 3. SEM cross-section micrograph of a CuSe/In₂Se₃ film after pressing and annealing at 600°C/20 min.

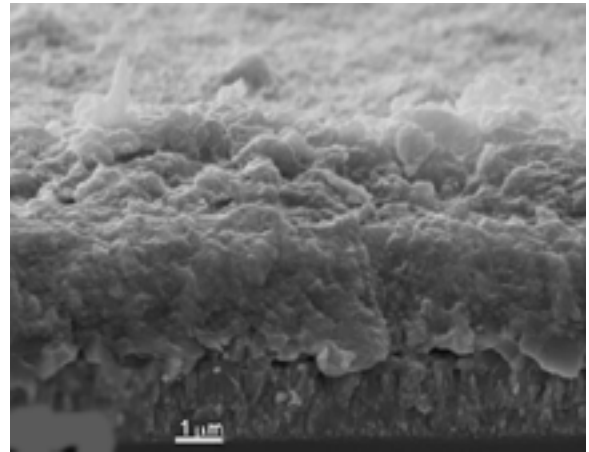


Fig. 4. SEM cross-section micrograph of a CIGS/CdS film as-sprayed at 225°C.

Approach 4: CIGS on CdS

In an example of serendipity, we observed the formation of a dense layer upon spraying CIGS colloid onto a CdS film. Accordingly, a Cu_{1.10}In_{0.68}Ga_{0.23}Se_x colloid was spray deposited onto a CdS/SnO₂/glass substrate at 225°C. This layered structure is amenable to a reverse backwall solar-cell approach. Figure 4 is an SEM micrograph of one such film where the CIGS layer appears to be very dense. Such dense layers have been previously reported for the chemical spray pyrolysis of CIS on CdS films; however, no thorough explanation of the phenomenon was reported [8]. XRD characterization of this as-sprayed film shows only peaks due to the substrate as determined in a control sample (i.e., CdS/SnO₂/glass). Even after annealing at 550°C/10 min under Ar, no reflections from the dense layer are observed; however, the CdS reflections decrease in intensity. Depth-profiled Auger data for the as-sprayed CIGS/CdS film shows a sharp interface

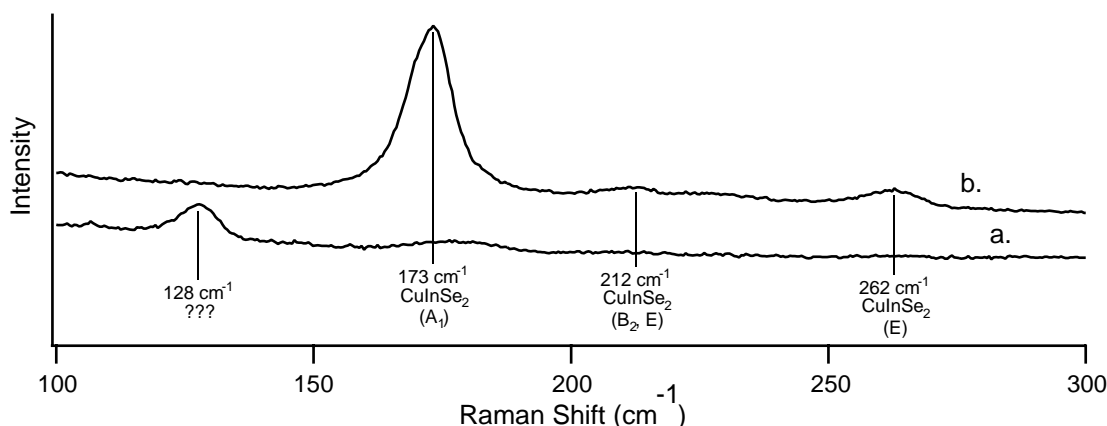


Fig. 2. Raman data for "CuInSe_{2.5}" films (a) as-sprayed at 225°C and (b) after annealing at 560°C/10 min.

with O detected throughout the film bulk region. After annealing at 550°C/10 min under Ar, Cd and S are observed to diffuse into the CIGS layer with a concomitant decrease in the O signal. This diffusion explains the decrease in the CdS intensity in the XRD after annealing. The mechanism of this growth phenomenon as well as a thorough characterization of these materials are underway.

CONCLUSIONS

Several approaches aimed at producing a dense CIS film from a porous precursor have been attempted. In these examples, bulk liquid-assisted growth is not observed. Spray deposition approaches using metal selenide starting materials may not afford a straightforward route to large-grained materials. A dense layer is observed upon spraying CIGS on CdS, however, the nature of this growth is not completely understood. Future directions include modification of the RTA approach to include one-side-only irradiation, RTA of the CuSe/In₂Se₃ composite, and elucidation of the growth mechanism responsible for the formation of dense layers in the CIGS-on-CdS system. Other possible directions include exploring the use of different nanoparticle precursor phases (e.g., Cu-In alloys, In₆Se₇/Cu, etc.) as well as utilizing different annealing strategies (e.g., processing in a sealed quartz tube with excess Se).

ACKNOWLEDGMENTS

The authors gratefully acknowledge Scot Albright for the gift of CdS/SnO₂/glass substrates. This research was funded by the U.S. Department of Energy, Office of Energy Research, Chemical Sciences Division and Materials Science Division and the U.S. Department of Energy National PV Program.

REFERENCES

- [1] D. L. Schulz, C. J. Curtis, R. A. Flitton, H. Wiesner, J. Keane, R. J. Matson, K. M. Jones, P. A. Parilla, R. Noufi, and D. S. Ginley, "Cu-In-Ga-Se nanoparticle colloids as spray deposition precursors for Cu(In,Ga)Se₂ solar cell materials," *J. Electron. Mater.* (submitted for publication).
- [2] J. R. Tuttle, J. S. Ward, A. Duda, T. A. Berens, M. A. Contreras, K. R. Ramanathan, A. L. Tennant, J. Keane, E. D. Cole, K. Emery, and R. Noufi, "The performance of CIGS-based solar cells in conventional and concentrator applications," *Mat. Res. Soc. Symp. Proc.* **426**, 1996, pp. 143-151.
- [3] F. J. Garcia and M. S. Tomar, "A screen printed cadmium sulfide/copper indium selenide solar cell," *Jpn. J. Appl. Phys., Part 1* **22**, 1983, pp. 535-538.
- [4] T. Arita, N. Suyama, Y. Kita, S. Kitamura, T. Hibino, H. Takada, K. Omura, N. Ueno, and M. Murozono, "Copper indium diselenide films prepared by screen-printing and sintering method," Twentieth IEEE PVSC, 1988, pp. 1650-1655.
- [5] C. J. Curtis, D. L. Schulz, R. A. Flitton, and D. S. Ginley, , pp. (manuscript in preparation).
- [6] V. Probst, F. Karg, J. Rimmasch, W. Riedl, W. Stetter, H. Harms, and O. Eibl, "Advanced stacked elemental layer process for CIGS thin film photovoltaic devices," *Mat. Res. Soc. Symp. Proc.*, **426**, 1996, pp. 165-176.
- [7] C. Rincón and F. J. Ramírez, "Lattice vibrations of CIS and CGS by Raman microspectroscopy," *J. Appl. Phys.* **72**, 1992, pp. 4321-4324.
- [8] B. J. Brown and J. C.W. Bates, "The effect of substrate on the morphology of CuInSe₂ films prepared by chemical spray pyrolysis for CuInSe₂/CdS solar cells," *J. Appl. Phys.* **68**, 1990, pp. 2517-2519.